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Executive Summary

Manitowoc Public Utilities (MPU) submitted two wipe samples of material collected from the porch of a nearby residence for analysis. The goal of the work was to analyze the composition of the black material collected on the wipe samples in order to determine its origin. The possibilities of what this material is include: dirt and/or sand, coal, petroleum coke, and CFB boiler ash.

The morphological analysis for the Wipe Sample 1/27/12 (MTI 12-021) shows several of the analysis spectra contained a large peak due to carbon. This carbon peak is not suitable for quantitation, but indicates the presence of carbon and/or organic material. Some analysis points consisted mainly of calcium and magnesium or just calcium. These compositions are consistent with limestone and/or dolomite material. It is possible that some particles could be derived from coal ash. If the material on the wipe came from dirt or sand, a predominance of silicon based mineral grains would be expected. If the materials have a petroleum coke origin, then one would expect to find vanadium and nickel present. The most abundant materials found appear to be limestone and dolomite derived particles.

The morphological analysis results for Wipe Sample 8/22/11 (MTI 12-022) show that many of the particles analyzed are consistent with limestone or dolomite materials. Some particles are mainly silicon indicating quartz; other particles contain calcium aluminum silicate and potassium aluminum silicate grains. These materials are consistent with sand materials. Distinct coal particles were not observed nor were petroleum coke particles. The coal particles would have had higher levels of sulfur and the petroleum coke particles would have had higher levels of vanadium or nickel than found in any of the analysis points. Carbon was present in many of the spectra indicating a carbon based material as the dark matrix. Limestone and dolomite particles appear to dominate the sample.

INTRODUCTION

Manitowoc Public Utilities (MPU) submitted two wipe samples of material collected from the porch of a nearby residence for analysis. The goal of the work was to analyze the composition of the black material collected on the wipe samples in order to determine its origin. The possibilities of what this material is include: dirt and/or sand, coal, petroleum coke, and CFB boiler ash. The samples are listed in Table 1.

Table 1. Samples submitted and analyses requested.

MTI Sample	Description	Analyses Requested				
12-021	Wipe Sample 1/27/12	Morphology				
12-022	Wipe Sample 8/22/11	Morphology				

METHODS

The wipe samples submitted were paper towels containing dark (black) material embedded on the towel. No loose or removable material was present. Sections of each sample containing the material in question were cut from the paper towels and mounted using double-stick carbon tape to a graphite planchet for SEM analysis. The mounted samples were coated with carbon for improved conductivity in the SEM. Morphological analysis was performed on the each of the wipe samples. Morphological analysis consists of obtaining images and chemical compositions of regions of interest. Images are taken using backscattered electron imaging, in which the brightness of a material is related to its average atomic number – higher atomic number materials such as silicates.

RESULTS AND DISCUSSION

The results of the morphological analysis for the Wipe Sample 1/27/12 (MTI 12-021) are presented in Table 2, with corresponding backscattered electron images presented in Figures 1 and 2. Several of the analysis spectra (those indicated) contained a large peak due to carbon. This carbon peak is not suitable for quantitation, but indicates the presence of carbon and/or organic material. Analysis points 1, 3, and 4 in Figure 1 and points 1, 2, and 5 in Figure 2 consisted mainly of calcium and magnesium or just calcium. These compositions are consistent with limestone and/or dolomite material. Particle 2 in Figure 1 contains mainly silicon, calcium, potassium and iron, with some aluminum and sulfur. Particle 6 in Figure 1 consists mainly of silicon, aluminum, potassium and calcium with some sulfur and iron present. Particle 3 in Figure 2 consists of silicon, calcium, and titanium with a small amount of iron. It is possible that Particle 6 and 3 could be derived from coal ash. If the material on the wipe came from dirt or sand, a predominance of silicon based mineral grains would be expected. If the materials have a petroleum coke origin, then one would expect to find vanadium and nickel present. The most abundant materials found appear to be limestone and dolomite derived particles.

Table 2. Morphological analysis results for Wipe Sample 1/27/12 (MTI 12-021). Results expressed as weight percent on an elemental basis, normalized to 100%.

Figure	Pt/Area	Description	Na	Mg	Al	Si	S	K	Ca	Ti	Fe	0
1	1 *	Particle	0.9	28.7	1.8	1.3	0.4	0.2	32.7	0.2	0.2	33.7
	2	Particle	0.2	0.1	2.2	61.6	2.0	7.7	11.1	0.8	12.7	1.7
	3 *	Light particle	2.0	20.7	2.2	1.8	0.5	0.2	13.9	0.1	0.3	58.3
	4 *	Particle	1.1	22.7	4.1	4.6	0.8	0.7	27.5	0.3	0.8	37.5
	5	Particle	0.0	17.3	1.6	53.2	1.0	0.5	0.9	0.2	1.6	23.8
	6	Particle	1.2	0.5	11.6	41.2	3.6	9.9	9.4	0.3	2.3	19.9
	7	Particle	0.4	0.2	0.1	0.1	0.1	0.1	0.1	0.1	98.5	0.2
	8	Bright particle	1.1	0.7	0.7	8.3	0.3	49.9	0.0	1.1	34.7	3.2
	9 *	Overall matrix	0.0	0.0	5.2	21.5	6.1	2.9	9.4	2.2	5.7	47.2
2	1	Particle	0.0	0.0	0.2	0.8	0.6	0.2	64.9	0.3	0.5	32.4
	2	Particle	0.5	0.4	0.2	0.2	0.2	0.2	88.6	0.7	3.0	5.9
	3	Bright particle	1.0	1.0	4.7	16.7	0.4	0.2	13.5	11.4	1.7	49.4
	4	Particle	0.5	0.7	2.9	48.0	0.8	0.7	0.2	0.1	0.6	45.6
	5	Bright particle	0.4	0.3	0.2	0.0	0.0	0.3	85.9	1.4	4.5	7.0
	6 *	Wipe fiber	1.0	2.4	8.8	29.9	11.5	5.4	6.8	3.0	5.9	25.3
	7 *	Overall matrix	0.4	0.7	4.3	12.5	4.0	2.1	8.0	2.4	5.2	60.6
	Average	All points	0.7	6.0	3.2	18.8	2.0	5.1	23.3	1.5	11.1	28.2

^{*}Spectra contained a large or significant carbon peak which was not quantified.

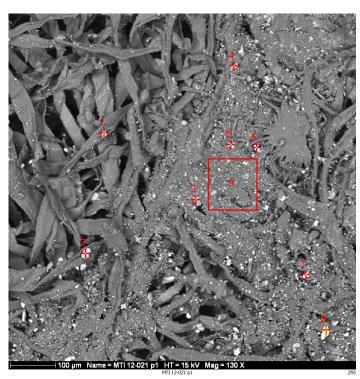


Figure 1. Backscattered electron image of Wipe Sample 1/27/12 (MTI 12-021), showing analysis points and areas 1 through 9.



Figure 2. Backscattered electron image of Wipe Sample 1/27/12 (MTI 12-021), showing analysis points and areas 1 through 7.

The morphological analysis results for Wipe Sample 8/22/11 (MTI 12-022) is found in Table 3. Micrographs showing the analysis points and areas are provided in Figures 3 and 4. Overall many of the particles analyzed (particles 1, 3, 4, and 5 in Figure 3 and particles 1, 2, 3, 6, and 7 in Figure 4) are consistent with a limestone or dolomite materials. Particles 2 and 6 in Figure 3 are mainly silicon indicating quartz. Particles 5 and 8 in Figure 4 contain calcium aluminum silicate and potassium aluminum silicate, respectively. These materials are consistent with sand materials. Distinct coal particles were not observed nor were petroleum coke particles. The coal particles would have had higher levels of sulfur and the petroleum particles would have had higher levels of vanadium or nickel than found in any of the analysis points. Carbon was present in many of the spectra indicating a carbon based material as the dark matrix. Limestone and dolomite particles appear to dominate the sample.

Table 3. Morphological analysis results for Wipe Sample 8/22/11 (MTI 12-022). Results expressed as weight percent on an elemental basis, normalized to 100%.

Fig.	Point	Description	Na	Mg	Al	Si	S	K	Ca	Ti	Fe	0
3	1	Particle	0.0	20.4	0.7	1.4	0.2	0.4	66.4	0.6	0.9	9.0
	2	Particle	1.5	1.0	0.8	75.5	1.7	1.4	1.8	3.1	7.1	6.1
	3	Particle	0.0	20.5	0.0	0.4	0.3	0.2	66.3	0.4	0.7	11.3
	4	Light particle	0.2	0.1	0.1	0.1	0.1	0.1	94.3	0.3	0.8	3.9
	5	Particle	0.5	4.7	0.0	0.0	0.2	0.0	87.3	0.7	1.8	4.8
	6	Particle	0.1	0.0	0.1	93.5	0.7	0.6	0.5	0.3	0.7	3.3
	7 *	Overall matrix	0.0	0.7	3.8	19.0	4.2	2.1	15.7	0.5	4.7	49.3
4	1	Particle	0.5	0.4	0.2	0.2	0.2	0.3	89.3	1.1	4.5	3.4
	2 *	Particle	0.3	26.2	1.6	0.8	0.5	0.2	41.6	0.3	0.7	27.8
	3 *	Particle	1.7	23.9	2.6	1.4	0.5	0.2	20.3	0.2	0.2	49.0
	4	Particle	1.5	0.9	0.6	0.4	0.5	0.4	9.4	0.7	83.4	2.3
	5 *	Particle	0.5	0.0	19.4	46.7	1.1	0.8	23.1	0.3	0.9	7.3
	6 *	Particle	0.9	23.6	2.2	1.5	0.6	0.2	29.6	0.3	0.3	40.7
	7 *	Particle	1.6	24.4	2.8	1.7	0.3	0.2	22.5	0.2	0.4	45.9
	8 *	Particle	0.2	0.2	21.3	47.0	0.8	22.0	0.6	0.3	3.4	4.3
	9 *	Overall matrix	0.0	1.2	3.0	19.6	4.5	1.8	14.9	0.4	5.7	49.1
	Average	All points	0.6	9.3	3.7	19.3	1.0	1.9	36.5	0.6	7.3	19.8

^{*}Spectra contained a large or significant carbon peak which was not quantified.

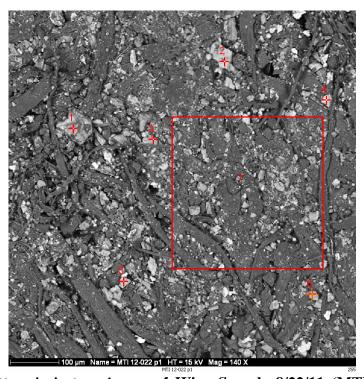


Figure 3. Backscattered electron image of Wipe Sample 8/22/11 (MTI 12-022), showing analysis points and areas 1 through 7.

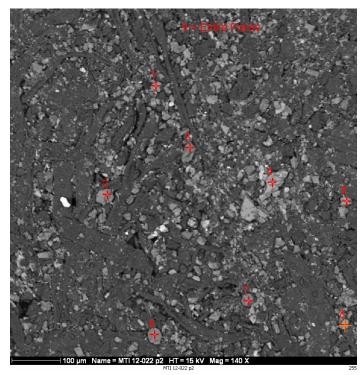


Figure 4. Backscattered electron image of Wipe Sample 8/22/11 (MTI 12-022), showing analysis points and areas 1 through 9.

SUMMARY

The morphological analysis for the Wipe Sample 1/27/12 (MTI 12-021) shows several of the analysis spectra contained a large peak due to carbon. This carbon peak is not suitable for quantitation, but indicates the presence of carbon and/or organic material. Some analysis points consisted mainly of calcium and magnesium or just calcium. These compositions are consistent with limestone and/or dolomite material. It is possible that some particles could be derived from coal ash. If the material on the wipe came from dirt or sand, a predominance of silicon based mineral grains would be expected. If the materials have a petroleum coke origin, then one would expect to find vanadium and nickel present. The most abundant materials found appear to be limestone and dolomite derived particles.

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